

COMPLEXES OF LEAD(II) PERCHLORATE AND HEXAFLUOROPHOSPHATE WITH AROMATIC AMINE N-OXIDES

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ABSTRACT: The syntheses of adducts of lead perchlorate and lead hexafluorophosphate with aromatic amine N-oxides are reported. The analytical data are consistent with the following formulas: $Pb(ClO_4)_2 \cdot 2(2\text{-picNO})$, $Pb(ClO_4)_2 \cdot 2(3\text{-picNO})$, $Pb(ClO_4)_2 \cdot 2(4\text{-picNO})$, $Pb(ClO_4)_2 \cdot 4(4\text{-OMepNO})$, $Pb(ClO_4)_2 \cdot 5(4\text{-NO}_2\text{pyNO})$, $Pb(ClO_4)_2 \cdot 6(4\text{-ClpyNO})$, $Pb(ClO_4)_2 \cdot 6(\text{pyNO})$, $Pb(PF_6)_2 \cdot 5(2\text{-picNO})$, $Pb(PF_6)_2 \cdot 5(3\text{-picNO})$, $Pb(PF_6)_2 \cdot 5(4\text{-picNO})$. The compounds were characterized by conductance in acetonitrile and nitromethane and by infrared spectroscopy. The infrared data suggest coordination of the perchlorate ion for 2-, 3- and 4-picNO and for 4-OMepNO complexes.

KEY-WORDS: Lead; coordinated perchlorate; aromatic amine N-oxide; complexes.

INTRODUCTION

Amine N-oxides act as electron-pair donors, forming molecular adducts and complexes with a variety of acceptor molecules, such as metal salts and complexes, halogens and organic compounds¹. The systematic synthetic and characterization studies of metal complexes of aromatic amine N-oxides were initiated in 1961² and since then a large number of publications have appeared in the literature. Three reviews^{1, 3, 4} covering the subject were published. Although several detailed reports concerning complexes of aromatic amine N-oxides with transition metals^{1, 3} have appeared, few work has been done involving these ligands and lead(II) ions⁵.

In this paper we report the adducts of lead perchlorate and hexafluorophosphate with 2 - picoline - N - oxide (2 - picNO), 3 - picoline - N - oxide (3 - picNO), 4 - picoline - N - oxide (4 - picNO), 4 - methoxypyridine - N - oxide (4 - OMepyNO), 4-chloropyridine-N-oxide (4-ClpyNO), 4-nitropyridine-N-oxide (4-NO₂pyNO) and pyridine-N-oxide (pyNO).

The compounds were characterized by elemental analysis, infrared spectroscopy and electrolytic molar conductance in acetonitrile and nitromethane. Considerations about coordination of perchlorate ions to the lead ion are presented.

EXPERIMENTAL

Materials

2 - picoline - N - oxide (Schuchardt) and 4 - picoline - N - oxide (Fluka) were recrystallized from acetone; 3 - picoline - N - oxide (Aldrich) was distilled under vacuum; 4-methoxypyridine-N-oxide was recrystallized from petroleum ether; pyridine-N-oxide and 4-nitropyridine-N-oxide were prepared and purified by the OCHIAI⁶ method and 4-chloropyridine-N-oxide was prepared by the method of HERTOG & COMBÉ⁷. Lead perchlorate was obtained by dissolution of a slight excess of lead carbonate in perchloric acid followed by filtration, concentration of the solution on a steam bath, crystallization and drying in vacuo over anhydrous calcium chloride. Ammonium hexafluorophosphate was purchased from Alpha. Other chemicals and solvents were always of analytical grade.

Preparation of the adducts

Adducts of lead perchlorate

The adducts were prepared by direct interaction of solutions of lead perchlorate and an excess of the ligands in absolute ethanol for 2-picNO, 4-picNO, 4-ClpyNO and 4-OMepyNO. Methanol and acetone were used as solvents for the preparation of the adducts of 4-NO₂pyNO and pyNO, respectively. Warmed solutions of salt and ligand in ethanol: triethyl orthoformate (1:1) were used to obtain the 3-picNO adduct. The solid compounds were filtered, washed with the corresponding solvent and dried in vacuo, over anhydrous calcium chloride.

Adducts of lead hexafluorophosphate

A concentrated aqueous solution of hexafluorophosphate, obtained in the same way as the lanthanide hexafluorophosphate⁸ aqueous solution, was diluted with absolute ethanol and treated with an ethanolic solution of 4-picNO or 3-picNO (molar ratio 1:10); with 2-picNO isopropanol was used as solvent. The precipitates were collected by filtration, washed with small portions of the corresponding alcohol and dried in vacuo over anhydrous calcium chloride.

Analytical procedure

Lead ion was determined by complexometric titration with EDTA⁹. Carbon and hydrogen were determined by microanalytical procedures. The absence of water was verified by infrared spectroscopy.

Measurements

Conductance measurements were made at 25,0±0,1°C using a Metrohm Konduktoskop E 365B and Metrohm cells (K₀=11,8 cm⁻¹ and 6,15 cm⁻¹). Infrared spectra were obtained in a Perkin-Elmer model 467 spectrophotometer using nujol mulls, between KBr plates. Melting ranges were determined in a Fisher-Johns melting point apparatus.

RESULTS AND DISCUSSION

The analytical results and melting ranges are summarized in Table 1. Some adducts melt with decomposition. They are soluble in acetonitrile, nitromethane, water and practically insoluble in acetone and methanol.

The electrolytic molar conductance data in acetonitrile and nitromethane are shown in Table 2. All the adducts behave as 1:2 electrolytes in these solvents according to GEARY¹⁰.

Infrared data are found in Table 3 and Figure 1 shows the infrared spectra of some compounds. The following aspects may be considered regarding the infrared data:

a) There are shifts in N-O (ν_{N-O}) stretching frequency for the complexed ligands to lower frequencies, in relation to the free ligands. These shifts are attributed to the coordination of aromatic amine-N-oxide to the metal through the oxygen atom, corresponding to an electron density decrease in the N-O bond of the ligand^{5, 11}. Absorptions in the range 870-840 cm⁻¹ have been assigned¹² to an NO bending (δ_{NO}) mode and are practically unaltered for most of the compounds, unless for a positive shift in the lead complex of 3-picNO. In the hexafluorophosphates complexes these bands are in the ν₃ frequencies region of the ionic hexafluorophosphate¹³ and therefore cannot be observed. Attempts to find correlations between the ν_{NO} frequencies shifts of the complexes with *σ*_{pyNO}¹¹ values of the ligands were not successful.

b) The free perchlorate ion belongs to the point group T_d and only ν₃ (~1080 - 1110 cm⁻¹) and ν₄ (~626 cm⁻¹) modes of vibration are expected to be infrared active. If the ion is coordinated to a metal, the symmetry is lowered and splittings of the degenerated modes occur (ν₃ and ν₄ are split in two or three bands corresponding to the coordination of one (C_{3v}) or two (C_{2v}) oxygen atoms)¹⁴. The ν₁ (~932 cm⁻¹) and ν₂ (460 cm⁻¹) modes corresponding to Raman active bands in the free ion are supposed to be infrared active upon coordination of perchlorate ion¹⁴. The lead

TABLE 2 - Electrolytic Conductance Data in Acetonitrile and Nitromethane

Compounds	Acetonitrile		Nitromethane	
	Conc. mM	Λ_M	Conc. mM	Λ_M
Pb(C ₁₀ H ₂) ₂ .2(2-picNO)	0.945	292	0.993	127
Pb(C ₁₀ H ₂) ₂ .2(3-picNO)	1.02	289	0.961	125
Pb(C ₁₀ H ₂) ₂ .2(4-picNO)	0.945	286	0.993	136
Pb(C ₁₀ H ₂) ₂ .4(4-OMepyNO)	0.982	263	0.993	162
Pb(C ₁₀ H ₂) ₂ .5(4-NO ₂ pyNO)	0.985	286	0.994	115
Pb(C ₁₀ H ₂) ₂ .6(4-ClpyNO)	1.04	260	0.972	144
Pb(C ₁₀ H ₂) ₂ .6(pyNO)	1.12	287	1.07	166
Pb(PF ₆) ₂ .5(2-picNO) ^a	0.978	320	—	—
Pb(PF ₆) ₂ .5(3-picNO) ^a	1.03	288	—	—
Pb(PF ₆) ₂ .5(4-picNO) ^a	1.03	304	—	—

$\Lambda_M = \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$

^a - In nitromethane these compounds are only slight solubles and the needed millimolar concentrations was not attained.

perchlorate complexes with 2-, 3- and 4-picNO show bands of medium intensity around 920 cm⁻¹ corresponding to the ν_1 mode of coordinated perchlorate. The ν_3 mode is split in two or three broad bands but the presence of the free ligand bands in this region precludes their analysis. The ν_4 mode is undoubtedly split in three bands for 2- and 3-picNO and in two bands for 4-picNO complexes. These splittings seem to be unequivocal for coordinated perchlorate ion¹⁴. In the region of the ν_2 mode, due to the occurrence of some free ligand bands, it is difficult to assign the bands to the perchlorate ion. These data plus the stoichiometries of the compounds are consistent with the coordination of perchlorate ion to the metal ion in those complexes. For the 4-NO₂pyNO and 4-OMepyNO complexes the ν_1 mode appears with weak intensity. For the 4-NO₂pyNO the ν_3 mode is split in three bands and the ν_4 mode in two bands. For 4-OMepyNO the ν_3 is split in two bands and ν_4 mode is not split. Again the stoichiometries and the infrared data suggest a coordination for the perchlorate ion, although not so evident as for the picNO complexes.

c) For the complexes with the hexafluorophosphate ion only single bands corresponding to ν_3 (~830 cm⁻¹) and ν_4 (~555 cm⁻¹) modes of the non-coordinated ion¹³ were observed. The two bands at 746 cm⁻¹ and 737 cm⁻¹ of medium intensity, corresponding to the ν_1 mode in 2-picNO complexes, look more like a crystal perturbation than a possible coordination.

A comparison of the stoichiometries and infrared data for the lead hexafluorophosphate and perchlorate with the aromatic amine oxide may suggest that

TABLE 1 - Summary of Analytical Results and Melting Ranges

COMPOUNDS	ANALYSIS (%)		Melting Ranges (°C)
	Found	Calc.	
Pb(C ₁₀ H ₂) ₂ .2(2-picNO)	33.17	33.18	250-252 dec.
Pb(C ₁₀ H ₂) ₂ .2(3-picNO)	33.18	32.81	216-220
Pb(C ₁₀ H ₂) ₂ .2(4-picNO)	33.18	33.14	235-237 dec.
Pb(C ₁₀ H ₂) ₂ .4(4-OMepyNO)	22.85	22.67	177-179
Pb(C ₁₀ H ₂) ₂ .5(4-NO ₂ pyNO)	18.72	18.21	169-171 dec.
Pb(C ₁₀ H ₂) ₂ .6(4-ClpyNO)	17.50	17.33	151-152 dec.
Pb(C ₁₀ H ₂) ₂ .6(pyNO)	21.21	21.01	149-151 dec.
Pb(PF ₆) ₂ .5(2-picNO)	19.87	20.10	88-90
Pb(PF ₆) ₂ .5(3-picNO)	19.87	19.37	194-196
Pb(PF ₆) ₂ .5(4-picNO)	19.87	19.93	149-151
Pb(C ₁₀ H ₂) ₂ .2(2-picNO)	23.08	23.08	Found
Pb(C ₁₀ H ₂) ₂ .2(3-picNO)	23.08	24.30	Found
Pb(C ₁₀ H ₂) ₂ .2(4-picNO)	23.08	23.44	Found
Pb(C ₁₀ H ₂) ₂ .4(4-OMepyNO)	31.80	32.17	Found
Pb(C ₁₀ H ₂) ₂ .5(4-NO ₂ pyNO)	27.14	26.97	Found
Pb(C ₁₀ H ₂) ₂ .6(4-ClpyNO)	30.45	31.42	Found
Pb(C ₁₀ H ₂) ₂ .6(pyNO)	36.89	36.44	Found
Pb(PF ₆) ₂ .5(2-picNO)	34.55	32.64	Found
Pb(PF ₆) ₂ .5(3-picNO)	34.55	34.82	Found
Pb(PF ₆) ₂ .5(4-picNO)	34.55	34.56	Found

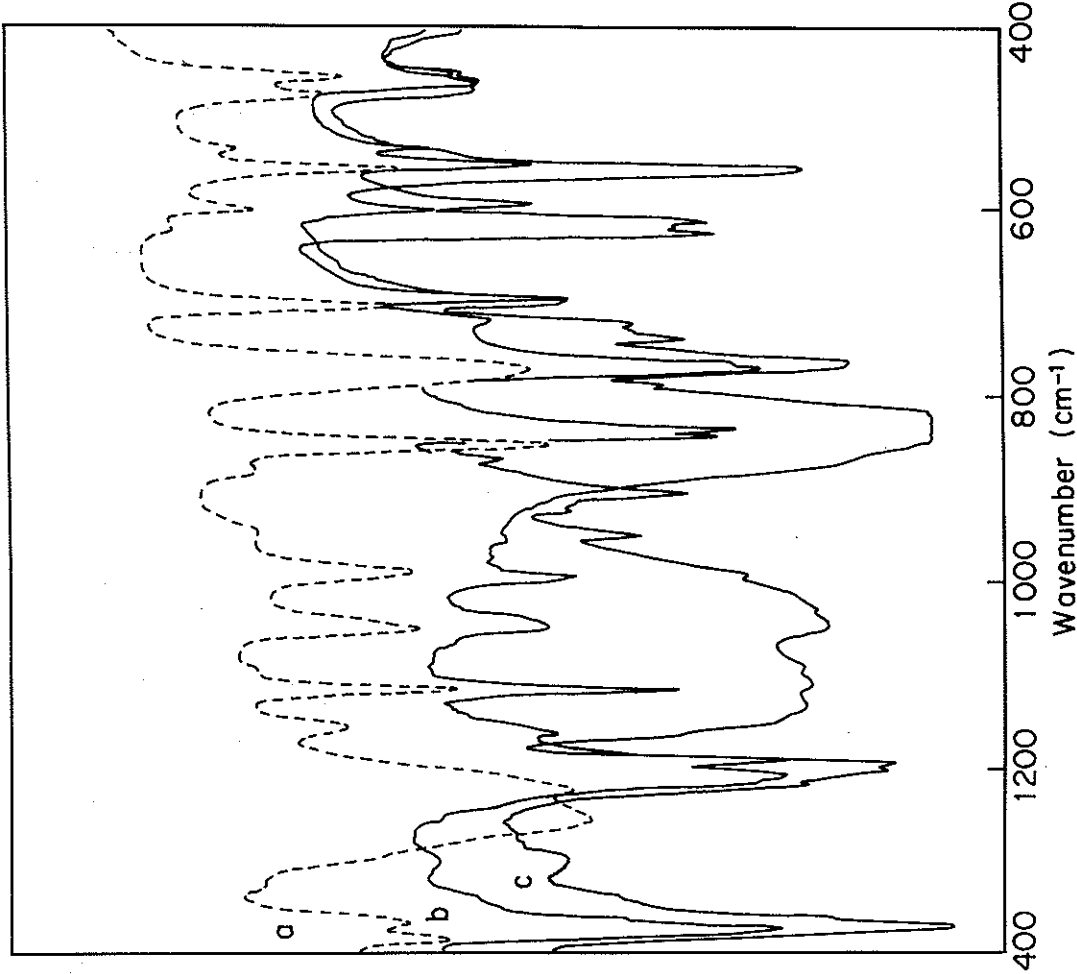


Fig. 1 - Infrared Spectra of: a) 2-picNO; b) Pb(C10₄)₂·2(2-picNO); c) Pb(PF₆)₂·2(2-picNO); d) Pb(C10₄)₂·2(4-ClpyNO). There is a strong evidence for coordination of perchlorate ion in the corresponding complexes of 2-, 3- and 4-picNO and a not so intense, but still evident, partial coordination in 4-OMepyNO and 4-NO₂pyNO complexes. A decision between a mono or a bidentate perchlorate ion is very difficult based on infrared data only and we prefer not to advance an answer for this question.

Some complexes, with different stoichiometries from the presented in this paper, were obtained during the course of our work by varying the solvents and the preparation conditions.

TABLE 3 - Infrared Data (cm⁻¹)

COMPOUNDS	P-N-O				C10 ₄				PF ₆			
	v ₁	v ₂	v ₃	v ₄	v ₁	v ₂	v ₃	v ₄	v ₁	v ₂	v ₃	v ₄
2-picNO	1252 vs	1217 s	850 vs	843s	-	913 m	1097s, 1037s	630s, 625br,	-	-	-	-
Pb(C10 ₄) ₂ ·2(2-picNO)	1211 vs	1278 vs,	1268 vs,	834 m	-	-	-	-	-	-	746m, 737m	843 br 562 s
Pb(PF ₆) ₂ ·5(2-picNO)	-	-	-	-	-	-	-	-	-	-	-	-
3-picNO	-	-	-	-	-	-	-	-	-	-	-	-
Pb(C10 ₄) ₂ ·2(3-picNO)	1264 s	1250 m	878 w	-	923 m	1130s, 1120s	630sh, 623s,	-	-	-	-	-
Pb(PF ₆) ₂ ·5(3-picNO)	1266 s	1253 sh	-	-	-	-	-	-	-	-	-	-
4-picNO	1252 s	1207 s	850 s	-	-	-	-	-	-	-	-	843 br 564 s
Pb(C10 ₄) ₂ ·2(4-picNO)	1224 s	1207 s	849 s	-	928 m	1143m, 1085s	623sh, 615s	-	-	-	-	-
Pb(PF ₆) ₂ ·5(4-picNO)	1224 s	1216 s	858 s	-	-	-	-	-	-	-	-	832s, br 565 s
4-OMepyNO	1216 s	1202 s	848 m, 838m	-	927vw	1115m, 1086s	618m	-	-	-	-	-
Pb(C10 ₄) ₂ ·4(4-OMepyNO)	1278 s	1278 s	878m, 868s	-	-	-	-	-	-	-	-	-
4-NO ₂ pyNO	1276 s	1276 s	878m, 868s	-	940 w	1146m, 1111s	636m, 626m	-	-	-	-	-
Pb(C10 ₄) ₂ ·5(4-NO ₂ pyNO)	1248 s	1248 s	848 m	-	-	-	-	-	-	-	-	-
4-ClpyNO	1226 s,	1226 s,	848 m	-	-	-	-	-	-	-	-	-
Pb(C10 ₄) ₂ ·6(4-ClpyNO)	1210 sh	848 m	-	-	-	-	-	-	-	-	-	-
Pb(C10 ₄) ₂ ·6(4-ClpyNO)	1265	840 s	-	-	-	-	-	-	-	-	-	-
Pb(C10 ₄) ₂ ·6(PyNO)	1250 s	840 s	-	-	-	-	-	-	-	-	-	-
Pb(C10 ₄) ₂ ·6(PyNO)	1250 s	840 s	-	-	-	-	-	-	-	-	-	-

vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder; br = broad

The results related suggest that the coordination of the perchlorate ion, in relation to the lead ion, could be changed by changing the solvent used in the preparations and that both perchlorate ion and the aromatic amine oxides employed compete for the coordination to the lead ion.

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CHIERICATO JUNIOR, G. *et alii* - Complexos de perclorato de chumbo (II) e hexafluorofosfato de chumbo(II) com aminóxidos aromáticos. *Ecl. Quím.* São Paulo, **14**: 49-56, 1989.

RESUMO: Descreve-se a síntese de adutos de perclorato de chumbo e hexafluorofosfato de chumbo com aminóxidos aromáticos. Os resultados analíticos são compatíveis com as seguintes fórmulas: $Pb(ClO_4)_2 \cdot 2(2\text{-picNO})$, $Pb(ClO_4)_2 \cdot 2(3\text{-picNO})$, $Pb(ClO_4)_2 \cdot 2(4\text{-picNO})$, $Pb(ClO_4)_2 \cdot 4(4\text{-OMepyNO})$, $Pb(ClO_4)_2 \cdot 5(4\text{-NO}_2\text{pyNO})$, $Pb(ClO_4)_2 \cdot 6(4\text{-ClpyNO})$, $Pb(ClO_4)_2 \cdot 6(pyNO)$, $Pb(PF_6)_2 \cdot 5(2\text{-picNO})$, $Pb(PF_6)_2 \cdot 5(3\text{-picNO})$, $Pb(PF_6)_2 \cdot 5(4\text{-picNO})$. Os compostos foram caracterizados por medidas de condutância em acetonitrila e nitrometano e por espectroscopia na região do infravermelho. Os dados do infravermelho sugerem a coordenação do íon perclorato nos complexos com 2-, 3-, 4-picNO e 4-OMepyNO.

UNTERMOS: Chumbo; complexos; perclorato coordenado; aminóxido aromático.

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